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HIGH DAMAGE THRESHOLD POROUS SILICA
ANTIREFLECTIVE COATING

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ABSTRACT

A quarterwave-thick, narrow-bandwidth, antireflective coating for fused silica optical components and KDP crystals has been developed. The coating consists of porous silica prepared from a silica sol in ethanol. It is applied by dip or spin from a solution at room temperature and requires no further treatment. The damage threshold levels are about equal to the surface damage thresholds of the uncoated substrates.

Introduction

For some time we have been investigating the use of porous silica as an antireflective (AR) coating for high power laser optics. The use of porous silica as an AR coating is well known; acid leaching, well summarized by Cook and Mader (1), acid neutralized sodium silicate (2), and silica sols (3) have all been used on glass substrates to produce films of varying degree of effectiveness. All of these are aqueous systems and use commercially available materials. Some work has also involved the use of organic silicates in organic solvents as the silica source (4, 5). These materials are readily hydrolyzed to silica and have been applied as acid-catalyzed, partially hydrolyzed products in organic solution to give porous coatings after exposure to water and heat:

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH$$

where R represents CH_3 or C_2H_5.

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Because of the special nature of coatings required for laser applications, particularly damage resistance, our investigation has involved the use of organic silicates, specifically tetraethyl orthosilicate, $Si(OC_2H_5)_4$, as the silica source. This material is a volatile liquid and can readily be purified by fractional distillation; the silica obtained by hydrolysis retains the high purity level and thus laser damage due to impurities is minimized.

The hydrolysis of tetraethyl silicate requires either an acidic or basic catalyst and the intermediate products are quite different in each case. The reactions are shown in Figure 1. With an acid catalyst a soluble poly-ethoxysiloxane is first formed; at this stage it can be applied to a substrate and subsequent heat treatment to 450 C, to decompose organic entities, followed by a mild HF etch gives a porous silica coating. When a base catalyst is used, a colloidal suspension of silica particles, completely free of organic entities, is formed and when this is applied to a substrate a porous silica coating of layers of silica particles is obtained with no further treatment.

Initially, we investigated the acid-catalyzed system, but had problems in some cases with the laser damage threshold being low, even though the AR properties were quite satisfactory. This laser damage was thought to be due to carbonaceous residues left in the coating from incomplete removal of organic material during the heat treatment. We then turned our attention to the base-catalyzed system, and this has given high damage thresholds and quite satisfactory optical performance. In addition, the coatings are much simpler to prepare and apply.

Fused silica focussing lenses of 80 cm diameter and 27 cm square potassium dihydrogen phosphate (KDP) crystals are now coated routinely with the coating solution described below.

Experimental

Tetraethyl orthosilicate was fractionally distilled using a 120 cm vacuum jacketed and silvered Vigreux glass column fitted with an infinitely variable distillation head. The fraction boiling at 166-167 C was collected for subsequent use.

The coating sol was prepared by the base catalyzed hydrolysis of the distilled product by a method similar to that described by Stober (6) as follows. Concentrated ammonium hydroxide solution (57% analytical reagent, 9.6 g) was added to a solution of tetraethyl silicate (31.2 g) in anhydrous ethyl alcohol (259 g) with stirring at room temperature. The reaction mixture was then allowed to stand at room temperature for three days to allow hydrolysis and sol formation to be completed. The final product consisted of a colloidal suspension of SiO_2 particles in substantially anhydrous ethanol at a concentration of 3.0%. Transmission electron microscopy indicated the silica particles were approximately spherical with a diameter of about 20 nm.

Coating was carried out either by a spin or dip process. Samples were coated at room temperature and then air dried; no further treatment was required. For AR coatings optimized for 350 nm wave length light, a withdrawal rate of 5 cm/min was suitable for the dip process. Spinning was carried out at 350 rpm and required ethanol dilution of the coating sol to 0.75% silica. Thicker coatings for longer wavelength light were obtained by multidip or spin with air drying in between.

The results described in the next section were obtained on 5 cm diameter by 1 cm thick polished fused silica substrates and on 5 cm x 5 cm x 1.75 cm KDP crystals with diamond turned surfaces. Larger samples are now routinely coated and their performance is similar to that reported for the smaller samples.

Discussion of Results

Transmission spectra of our coatings on fused silica and KDP substrates are shown in Figs. 2 and 3. These spectra are characteristic of quarterwave AR coatings of refractive index corresponding to the relationship $n_c = \sqrt{n_1 n_2}$ where n_c is the index of the coating, n_1 is the index of air, and n_2 is the index of substrate. Appropriate substitution indicates that the index of the coating is approximately 1.22. Further calculation then shows that the silica particles must be stacked to give an average porosity of about 50%.

It is interesting to note that the densest possible packing of uniform spheres gives a porosity of only 26%. We must therefore conclude that the slight variations in particles size and shape and also possible particle porosity contribute to the increased porosity of coatings obtained from them.

The effect of multicoats on fused silica substrates is also illustrated in Fig. 2. The transmission maximum of the first coat is masked by absorption of the substrate; the second and third coats however show that thickness is additive, and in this case calculations indicate that each coat is approximately 39 nm thick (46 nm optical thickness). As the particle size is only about 20 nm, each coat is only two particle layers thick.

We have found that thicker coatings can also be obtained by increasing the silica content in the coating sol, as might have been expected.

Figure 4 gives laser damage thresholds measured at three different laser wavelengths and pulse durations for the sol coatings on fused silica substrates, and that measured at one laser wavelength for the coatings on KDP substrates. The 248-nm threshold was measured by Foltyn at Los Alamos National Laboratory. These thresholds were measured on coatings whose thicknesses were arranged such that maximum transmission occurred at the measurement wavelengths. The thresholds obtained approximate to the thresholds measured for the uncoated substrate surfaces.

Summary

A method has been developed to prepare porous silica AR coatings on silica or KDP substrates. This involves the preparation of a silica sol in ethanol from a high purity organic silicate starting material and application of this sol, by spin or dip, to substrates at room temperature followed by an air dry. No further processing is required and coatings with high laser damage thresholds and excellent optical performance are obtained.

References

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Figure Captions

1. Hydrolysis of tetraethyl silicate.
2. Transmittance of coatings on fused silica substrates.
3. Transmittance of coatings on diamond-turned KDP substrates.
4. Laser damage thresholds.

Hydrolysis of T.E.O.S.

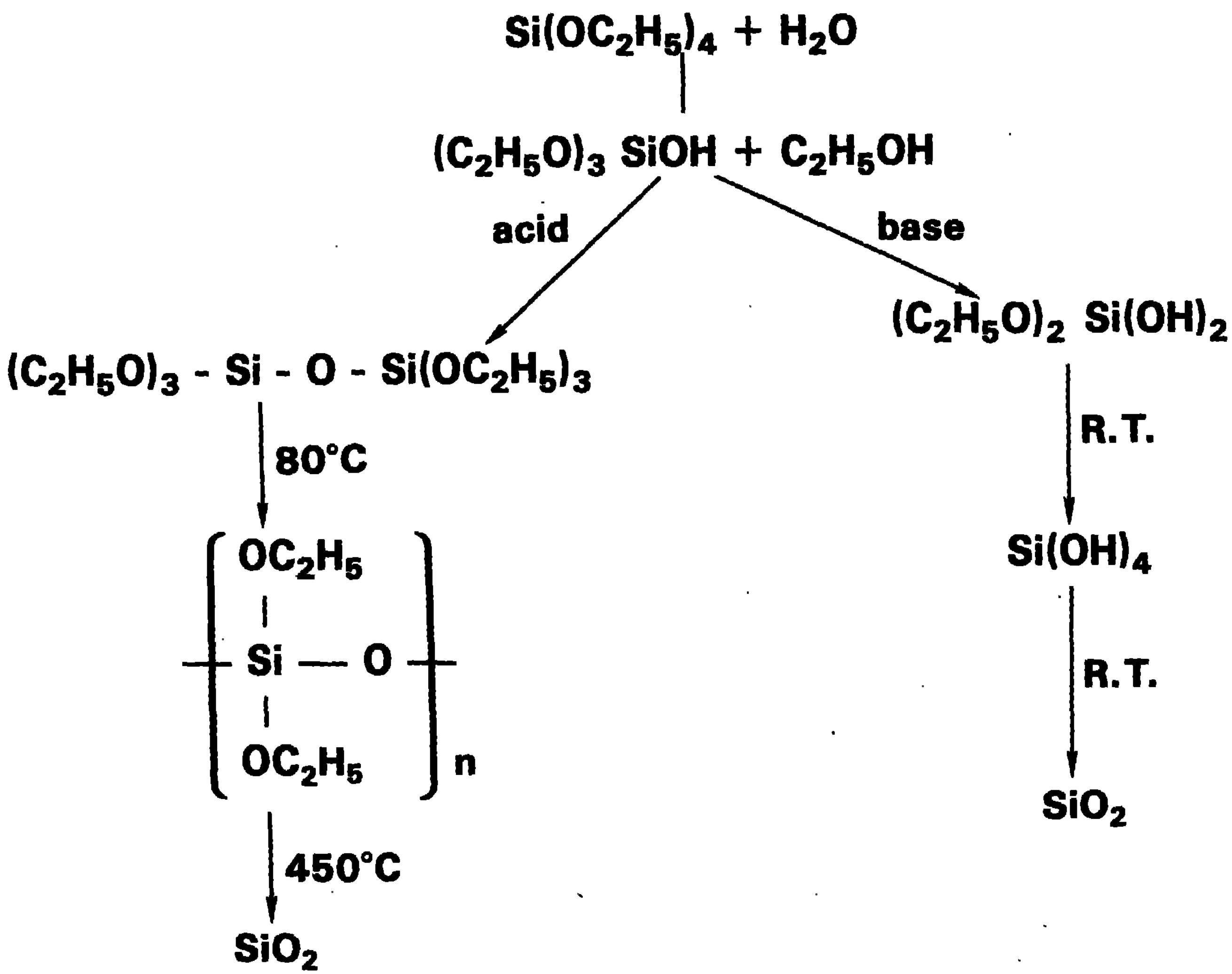

Figure 1

Transmission spectrum of porous silica HR coating on fused silica is controlled by coating's thickness

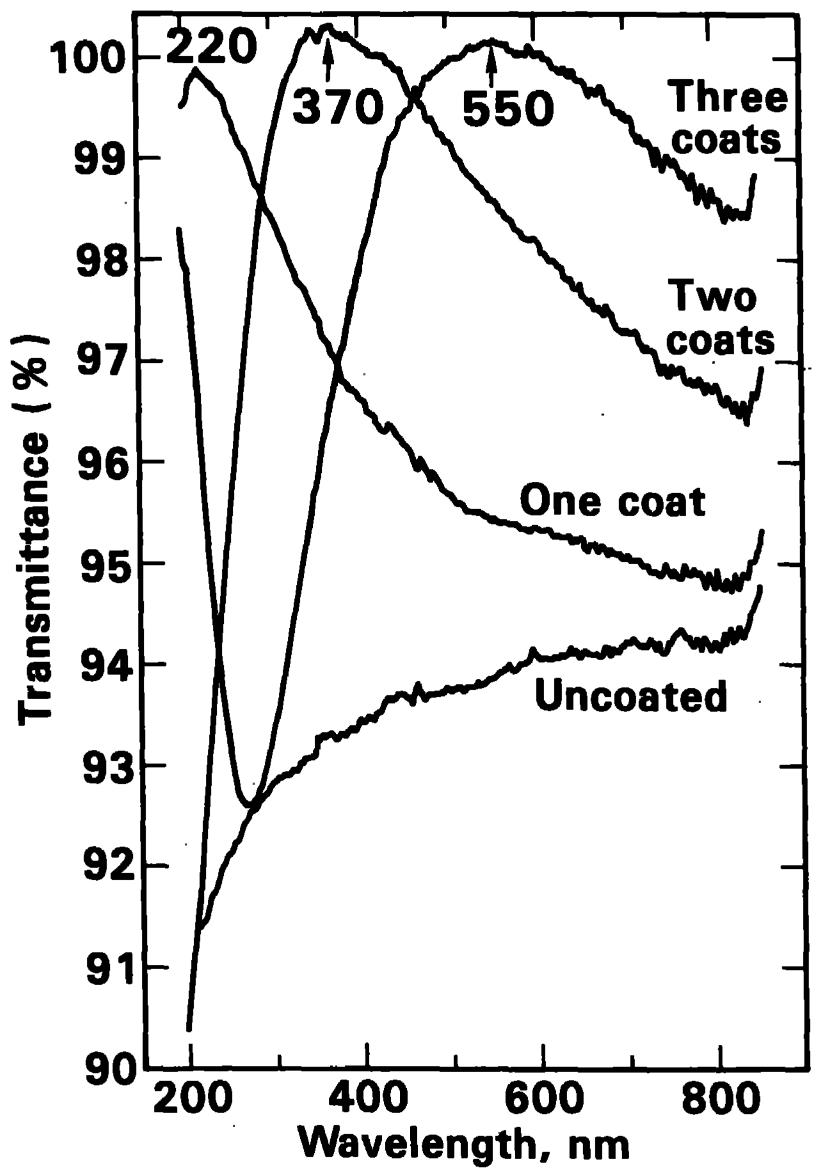

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Figure 2

Transmission of KDP

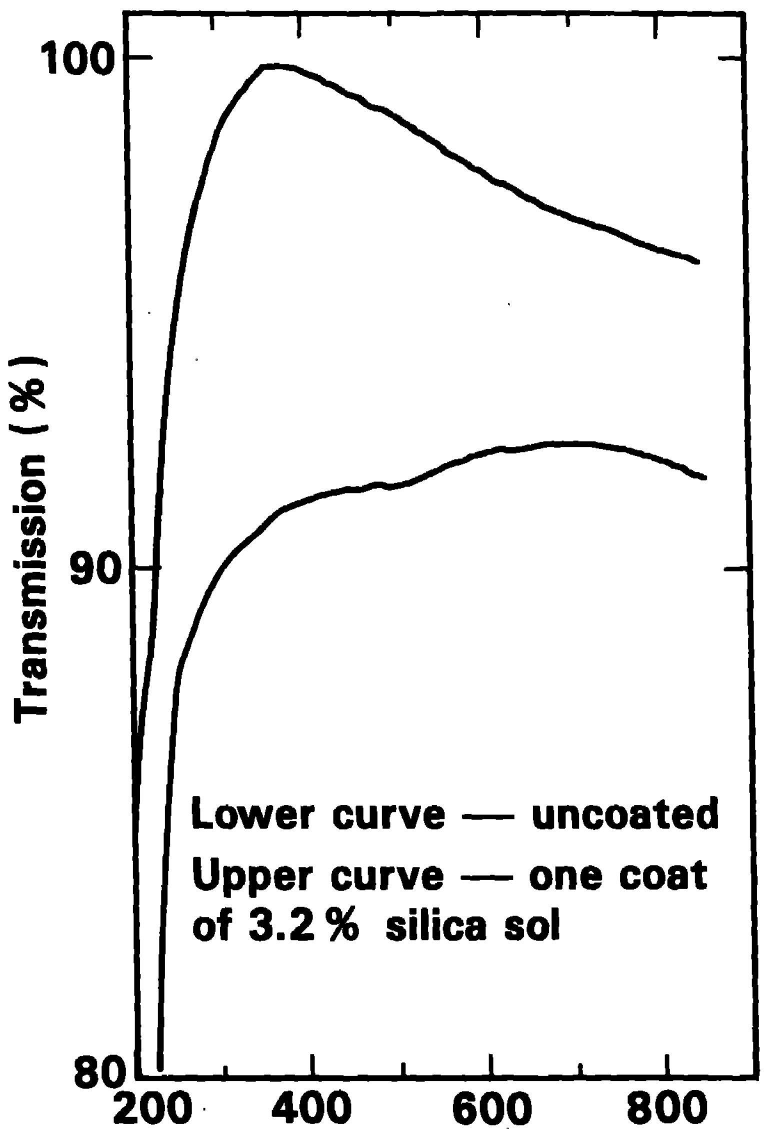

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Figure 3

Laser Damage Thresholds

Laser	SiO_2 substrate	KDP substrate
248 nm, 15 ns pulse	4 - 5 J/cm^2	
355 nm, 0.6 ns pulse	8.5 - 10 J/cm^2	> 4 - 5 J/cm^2
1064 nm, 1.0 ns pulse	10 - 14 J/cm^2	

Figure 4